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ARRHENIUS SYSTEMS: DYNAMICS OF JUMP DUE TO SLOW PASSAGE THROUGH--ETC(U)

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ARRHENIUS SYSTEMS:
DYNAMICS OF JUMP DUE TO
SLOW PASSAGE THROUGH CRITICALITY

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10 A. K. Kapila*

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ABSTRACT

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Reactive systems involving Arrhenius kinetics often exhibit multiple steady states. A typical response is an S-curve, whose turnaround points correspond to ignition or extinction. This paper describes the dynamics of transition from the extinguished to the ignited state as the reaction-rate parameter is slowly varied through the critical value. Both lumped and spatially distributed models are studied. The asymptotic analysis is based on the largeness of two parameters: one characterizing the activation energy and the other the slow passage.

AMS (MOS) Subject Classifications: 35K22, 80A25

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SIGNIFICANCE AND EXPLANATION

Exothermic chemistry involving Arrhenius kinetics is of practical importance in combustion as well as chemical engineering. Arrhenius systems often exhibit multiple steady states; a typical stationary response is an S-curve. From such a steady response it is often argued that the system would jump from a weakly reactive, almost extinguished state to one of vigorous chemical activity as a control parameter (e.g. the Damkohler number) is increased through a critical value. A similar jump from ignition to extinction is implied as the control parameter is reduced through a different critical value. Thus, inherently transient pictures are inferred from steady solutions.

The purpose of this study is to provide an unsteady description of the jump phenomena. Attention is focussed on situations where the variation of the control parameter through criticality is gradual. Such variations might correspond, in practice, to a slow deterioration in the activity of a catalyst or to slow increase in pressure. The asymptotic analysis also makes use of large activation energy.

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ARRHENIUS SYSTEMS: DYNAMICS OF JUMP DUE TO
SLOW PASSAGE THROUGH CRITICALITY

A. K. Kapila^{*}

1. INTRODUCTION

Reactive systems involving Arrhenius chemistry abound in several areas of practical interest, ranging from chemical-reactor engineering to combustion. Often, such systems exhibit multiple steady states. Typically, the equilibrium plot of a state variable y (e.g. the maximum temperature) against a control variable ϕ , measuring the reaction rate, is an S-curve (Figure 1). The lower branch of the S represents the low-conversion or extinguished state while the upper branch corresponds to the high-conversion or ignited state. In many cases both of these branches are asymptotically stable while the middle branch is unstable, the exchange of stabilities occurring precisely at the turnaround points of the S. The steady states and their stability are discussed in great detail by Aris [1,2] in the context of diffusion and reaction in permeable catalyst pellets. The forthcoming monograph by Buckmaster and Ludford [3] will provide several relevant examples from combustion.

This paper is concerned with the dynamic response of the system to slow variations in ϕ . Such variations may be due, in practice, to changes in pressure or in catalytic efficiency. Imagine, for example, that the system is initially in equilibrium at an extinguished state, such as that corresponding to point A in Figure 1. If ϕ is now increased gradually, it is expected that the system will, more or less, follow the lower branch until the critical point (i.e. the ignition point) C is reached. Then, a jump to the ignited state will occur. The aim of this paper is to describe this

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transient process. A similar but simpler analysis, not presented here, describes the jump from the ignited to the extinguished state due to slow passage through the extinction point E .

For lumped systems, governed by nonlinear ordinary differential equations of type $dy/dt = F(y;\phi)$, the response due to slow variations in ϕ has recently been examined by Haberman [4]. He looks, in particular, at a neighborhood of the critical point C and shows that there exists a transition region which connects the near-equilibrium pre-critical solution (in which ϕ is slowly varying) to the jump solution (in which ϕ is stationary at ϕ_c). For those cases in which the S-curve is parabolic near C , Haberman shows further that the aforementioned transition region is governed by a Riccati equation whose solution explodes in a finite time. We shall extend these notions to show that an entirely analogous situation exists for the distributed system, governed by a partial differential equation.

This paper complements earlier investigations by Kapila [5] and by Kassoy and Poland [6,7] on the dynamics of ignition in distributed systems, and by Kassoy [8] on similar problems in lumped systems. There the emphasis was on evolution at fixed ϕ , while the present work treats time-varying ϕ . However, the earlier analyses are quite relevant here, as we shall see. Slow-transition problems for partial differential equations have also been considered by Rubinfeld [9], but only for bifurcation points rather than jump points. Buckmaster's treatment of slowly-varying flames [10] also falls in the former category.

Our analysis will be asymptotic, depending upon the largeness of two parameters, one characterizing the slow variation of ϕ and the other the activation energy of the reaction. A lumped model is treated first; it employs Haberman's idea in a slightly amplified form and lays the groundwork for the subsequent analysis of a distributed model.

2. A LUMPED MODEL

As an example of a lumped system, consider the Continuously Stirred Tank Reactor, CSTR, modelled by the equation [2]

$$y_\tau = \lambda^2(1+\beta-y) \exp(\gamma-\gamma/y) + 1-y, \quad (2.1)$$

where y is the temperature and τ the time, while the positive parameters λ^2, β and γ are, respectively, the Damkohler number, the heat of reaction and the activation energy. It is convenient to define a reduced Damkohler number ϕ via the transformation

$$\lambda^2 = (e\beta\gamma)^{-1}\phi. \quad (2.2)$$

It is known [2] that for large enough γ the equilibrium plot of y against ϕ has an S-shape (Figure 1), with the middle branch unstable and the extreme branches asymptotically stable. A straightforward analysis of the static problem ($y_\tau = 0$ in (2.1)) in the limit $\gamma \rightarrow \infty$ further shows that on the lower branch of the S the expansions

$$y = 1 + \gamma^{-1}y_1 + O(\gamma^{-2}), \quad \phi = \phi_1 + O(\gamma^{-1}) \quad (2.3)$$

hold, where the monotonically increasing function

$$y_1 = G(\phi_1), \quad 0 \leq \phi_1 \leq 1 \quad (2.4)$$

is defined implicitly by

$$y_1 = \phi_1 \exp(y_1 - 1), \quad 0 \leq y_1 \leq 1 \quad (2.5)$$

and is shown in Figure 2. The ignition point C corresponds to

$$\phi_1 = y_1 = 1 \quad \text{at C}.$$

Also, for future use we note that

$$G(\phi_1) = 1 - [2(1-\phi_1)]^{1/2} + \frac{2}{3}(1-\phi_1) + O[(1-\phi_1)^2] \text{ as } \phi_1 \rightarrow 1^- . \quad (2.6)$$

An analogous description of the upper branch yields

$$y_D = 1 + \beta - \text{est} \quad (2.7)$$

where est stands for terms that are exponentially small as $\gamma \rightarrow \infty$, and the point D on the upper branch is vertically above C .

Of interest is the dynamic behavior of y as ϕ varies slowly through ϕ_C . This slow variation can be characterized explicitly by introducing a small parameter δ and a slow time t , where

$$t = \delta\tau, \quad \delta \ll 1 ,$$

thereby transforming (2.1) into

$$\delta y_t = (e\beta\gamma)^{-1} \phi (1+\beta-y) \exp(\gamma-\gamma/y) + 1-y . \quad (2.8)$$

At an initial time $t = t_A < 0$, let the state of the system correspond to point A in Figure 1, i.e. let

$$y(t_A) = y_A , \quad \phi(t_A) = \phi_A .$$

Then, the expansions (2.3) imply that

$$y(t_A) = 1 + \gamma^{-1} y_{1A} + O(\gamma^{-2}), \quad \phi(t_A) = \phi_{1A} + O(\gamma^{-1}) . \quad (2.9)$$

Following (2.3) again, we let

$$\phi(t) = \phi_1(t) + O(\gamma^{-1}) \quad (2.10)$$

and assume that $\phi_1(t)$ is a smooth, monotonically increasing function which has the power series representation

$$\phi_1(t) = 1 + t + O(t^2) \text{ as } t \rightarrow 0 . \quad (2.11)$$

This specifies $t = 0$ to be the instant at which the ignition point is reached; there is no loss of generality in setting $\phi_1'(0) = 1$. The goal is to obtain an asymptotic solution to (2.8-2.9), with $\phi_1(t)$ prescribed above, in the limit $\delta \rightarrow 0, \gamma \rightarrow \infty$. Several different regimes need to be distinguished.

2.1 Pre-critical Solution

Anticipating that the solution stays close to unity until C is reached (i.e. until $t = 0$), we substitute

$$y = 1 + \gamma^{-1} z(t) \quad (2.12)$$

into (2.8) and expand for $\gamma \rightarrow \infty$ to get

$$\delta z_t = \phi_1 \exp(z-1) - z + O(\gamma^{-1}) \quad , \quad (2.13)$$

where (2.10) has also been employed. Henceforth the analysis will concentrate on the limit

$$\delta \gg \gamma^{-1} \quad . \quad (2.14)$$

The apparently richer limit $\delta = O(\gamma^{-1})$ can also be treated, at the simple expense of more algebra, but was found to yield no additional significant effect.

We let z have the expansion

$$z = z_1 + \delta z_2 + o(\delta) \quad (2.15)$$

which, when fed into (2.13), gives

$$z_1 = \phi_1 \exp(z_1 - 1) \quad , \quad (2.16)$$

$$z_2 = z_1' / (z_1 - 1) \quad , \quad (2.17)$$

where primes stand for differentiation with respect to t . Comparison of (2.16) with (2.5) shows that z_1 has the same form as the static solution (2.4), i.e.

$$z_1 = G(\phi_1(t)) \quad . \quad (2.18)$$

The asymptotic expressions (2.6) and (2.11) then show that, as expected, (2.18) is valid only for $t < 0$. In fact, we find that

$$z_1 = 1 - (-2t)^{1/2} - \frac{2}{3}t + O(-t)^{3/2} \quad \text{as } t \rightarrow 0^- \quad . \quad (2.19)$$

Once z_1 is known, (2.17) determines z_2 and we get the asymptotic behavior

$$z_2 = (2t)^{-1} + \frac{1}{3}(-2t)^{-1/2} + O(1) \quad \text{as } t \rightarrow 0^- \quad . \quad (2.20)$$

The above expression exhibits even more dramatically the breakdown of the pre-critical expansion (2.15).

A word about the initial conditions (2.9) is in order. These imply that $z_1(t_A) = y_{1A}$ and $z_2(t_A) = 0$. While z_1 , as given by (2.18), satisfies this requirement, z_2 , as given by (2.17), does not, in general. This discrepancy is easily remedied by means of a thin initial layer at t_A in which the relevant time is the fast time τ . In this layer, the effect of the initial condition on z_2 decays exponentially rapidly. In fact, even initial conditions off the lower branch can be accommodated in this manner provided, of course, that the initial point lies within the domain of attraction of the (asymptotically stable) lower branch.

2.2 Transition Solution

Further development of the solution occurs on a new time scale s , defined by the stretching

$$t = -2^{1/3} \delta^{2/3} s . \quad (2.21)$$

The new time is short on the t scale but is still long, $O(\delta^{-1/3})$, on the τ scale. Equations (2.11) and (2.13) transform into

$$\phi_1 = 1 - 2^{1/3} \delta^{2/3} s + O(\delta^{4/3}) \quad (2.22)$$

and

$$-2^{-1/3} \delta^{1/3} z_s = [1 - 2^{1/3} \delta^{2/3} s + O(\delta^{4/3}) + O(\gamma^{-1})] \exp(z-1) - z + O(\gamma^{-1}) , \quad (2.23)$$

and the new expansion for z is taken to be

$$z = 1 + \delta^{1/3} v_1(s) + \delta^{2/3} v_2(s) + O(\delta) . \quad (2.24)$$

It is clearly shown by (2.22) and (2.24) that the transition solution is restricted to a small neighborhood of the critical point C . Substitution of (2.24) into (2.23) yields the following Riccati equation for v_1 :

$$v_1' = 2^{1/3} (2^{2/3} s - \frac{1}{2} v_1^2) , \quad s < \infty . \quad (2.25a)$$

The condition

$$v_1 \rightarrow -2^{2/3} (s^{1/2} + \frac{1}{2s}) \quad \text{as } s \rightarrow \infty \quad (2.25b)$$

comes from matching (2.24) with the pre-critical solution. The solution to (2.25a,b) is (see [4])

$$v_1 = 2^{2/3} \text{Ai}'(s)/\text{Ai}(s) , \quad (2.26)$$

where Ai is the Airy function. This solution is valid only for $s > s_0$,

where $s_0 = -2.3318$ is the first zero of $\text{Ai}(s)$, and there it has the

explosive behavior

$$v_1 = 2^{2/3} [(s-s_0)^{-1} + \frac{1}{3} s_0 (s-s_0)] \quad \text{as } s \rightarrow s_0^+ . \quad (2.27)$$

This singularity immediately signals the breakdown of the transition solution and suggests that the solution is attempting to deviate from criticality farther than is allowed by the expansion (2.24). Before proceeding to the next regime, however, it is desirable to compute v_2 as well. The problem for v_2 is found to be

$$\begin{aligned} v_2' &= -2^{1/3} (v_1 v_2 + \frac{1}{6} v_1^3 - 2^{1/3} s v_1), \quad s < \infty, \\ v_2 &\rightarrow \frac{2^{1/3}}{3} (2s + \frac{1}{2} s^{-1/2}) \quad \text{as } s \rightarrow \infty, \end{aligned} \quad (2.28)$$

whence

$$\begin{aligned} v_2 &= 2^{1/3} \left\{ s + \{Ai(s)\}^{-2} \int_s^\infty \{Ai(x)\}^2 dx \right. \\ &\quad \left. + \frac{2}{3} \{Ai(s)\}^{-2} \int_s^\infty \{Ai'(x)\}^3 \{Ai(x)\}^{-1} dx \right\}, \end{aligned} \quad (2.29)$$

and it has the asymptotic behavior

$$v_2 \sim -\frac{2^{4/3}}{3} (s-s_0)^{-2} \ln(s-s_0) + A_0 (s-s_0)^{-2}, \quad \text{as } s \rightarrow s_0^+. \quad (2.30)$$

The constant A_0 is given by

$$\begin{aligned} A_0 &= 2^{1/3} \{Ai'(s_0)\}^{-2} \left\{ \frac{2}{3} \left\{ \int_0^\infty \{Ai'(x)\}^3 \{Ai(x)\}^{-1} dx \right. \right. \\ &\quad \left. + \int_{s_0}^0 (\{Ai'(x)\}^3 \{Ai(x)\}^{-1} - \{Ai'(s_0)\}^2 (x-s_0)^{-1}) dx \right. \\ &\quad \left. \left. + \{Ai'(s_0)\}^2 \ln(-s_0) \right\} + \int_{s_0}^\infty Ai^2(x) dx \right\}. \end{aligned} \quad (2.31)$$

2.3 Post-Critical Solution

The manner in which (2.24) breaks down suggests the stretching

$$s = s_0 - 2^{-1/3} \delta^{1/3} (\rho - \rho_0) \quad (2.32)$$

where the new time scale ρ is of the same order as the fast time τ , and the shift ρ_0 , assumed to be $O(\delta^{-1/3})$, is to be determined. The expression (2.22) reduces to

$$\phi_1 = 1 - 2^{1/3} \delta^{2/3} s_0 + \delta(\rho - \rho_0) + O(\delta^{4/3}) ,$$

indicating that ϕ remains close to (but larger than) the critical value, while (2.23) transforms into

$$z_\rho = [1 + O(\delta^{2/3})] \exp(z-1) - z + O(\delta) + O(\gamma^{-1}) .$$

We note that the unsteady term z_ρ now appears to leading order. Allowing z to have the expansion

$$z = w_1(\rho) + o(1) , \quad (2.33)$$

w_1 is found to satisfy

$$w_1' = \exp(w_1-1) - w_1 , \quad \rho > -\infty ,$$

yielding the implicit solution

$$\int_2^{w_1} [\exp(x-1) - x]^{-1} dx = \rho - \bar{\rho}_0 . \quad (2.34)$$

The integration constant $\bar{\rho}_0$ is to be determined. It can be shown that

$$w_1 \sim 1 - \frac{2}{\rho} - \frac{4}{3\rho^2} \ln(-\rho) + \frac{A_1}{\rho^2} \text{ as } \rho \rightarrow -\infty ,$$

where

$$A_1 = \frac{4}{3} \ln 2 - 4 - 2\bar{\rho}_0 + 2 \int_1^2 [\{\exp(x-1) - x\}^{-1} - 2(x-1)^{-2} + \frac{2}{3}(x-1)^{-1}] dx \quad (2.35)$$

Matching with the transition solution (2.24) yields

$$\rho_0 = -\frac{2}{9} \ln(\delta) \quad ,$$

confirming the expectation that $\rho_0 = o(\delta^{-1/3})$, and

$$A_1 = 2^{2/3} A_0 + \frac{4}{9} \ln 2 \quad .$$

With A_0 known from (2.31), substitution of the above expression into (2.35) will determine $\bar{\rho}_0$.

At this stage it is convenient to revert to the original dependent variable y . Substitution of (2.33) into (2.12) yields the expansion

$$y = 1 + \gamma^{-1} w_1(\rho) + o(\gamma^{-1}) \quad , \quad (2.36)$$

indicating that so far y has stayed close to unity. However, larger departures from unity are imminent, because the solution (2.34) for w_1 explodes in a finite time. In fact, (2.34) shows that w_1 increases monotonically and has the behavior

$$w_1 = -\ln(\rho_\infty - \rho) + 1 + o(1) \quad \text{as } \rho \rightarrow \rho_\infty \quad , \quad (2.37)$$

where

$$\rho_\infty = \bar{\rho}_0 + \int_2^\infty [\exp(x-1) - x]^{-1} dx \quad . \quad (2.38)$$

2.4 Jump Solution

The singularity (2.37) implies that (2.36) is no longer valid, and that further development of the solution takes place on the exponentially fast time scale σ , defined by the nonlinear stretching

$$\rho = \rho_{\infty} - \exp(-\gamma\sigma) \quad , \quad \sigma > 0 \quad .$$

On the σ scale, (2.10) reduces to

$$\phi = 1 - 2^{1/3} \delta^{2/3} s_0 + \delta[\rho_{\infty} - \rho_0 - e^{-\gamma\sigma}] + O(\delta^{4/3}) + O(\gamma^{-1}) \quad ,$$

indicating that ϕ undergoes only exponentially small variations from a fixed value in a $\delta^{2/3}$ -neighborhood of criticality. Therefore Kasoy's supercritical analysis [8], carried out for fixed ϕ , becomes relevant. We shall not repeat the details here; suffice it to say that the solution has the expansion

$$\gamma = (1-\sigma)^{-1} + O(\gamma^{-1})$$

and that γ reaches the upper-branch value $1 + \beta$ (cf. (2.7)) at $\sigma = \beta/(1+\beta)$, i.e. at

$$t = -2^{1/3} \delta^{2/3} s_0 + \delta[\rho_{\infty} - \rho_0 - \exp\{-\gamma\beta/(1+\beta)\}] \quad .$$

We note that during this exponentially rapid ascent, the governing parameter is γ ; hardly any role is played by δ . However, once the upper branch has been reached, further evolution of the solution, involving slow variation about the upper-branch equilibrium, will be governed by a δ -expansion analogous to (2.15).

3. A DISTRIBUTED MODEL

As an example of distributed systems, consider the porous catalyst pellet, for unit Lewis number and in the symmetric slab geometry, governed by the equations [1]

$$y_\tau = y_{xx} + \lambda^2 (1 + \beta - y) \exp(\gamma - \gamma/y), \quad 0 < x < 1, \quad (3.1a)$$

$$y_x(0, \tau) = 0, \quad y(1, \tau) = 1, \quad (3.1b)$$

with appropriate initial condition. The symbols have the same meanings as in Section 2; the new independent variable x denotes the spatial coordinate. It is again convenient to eliminate λ in favor of ϕ through the relation

$$\lambda^2 = (\beta\gamma)^{-1} \phi. \quad (3.2)$$

The relevant static problem, which is a classic in the chemical engineering literature [1], was recently studied by Kapila and Matkowsky (see the Appendix of [11]) in the limit $\gamma \rightarrow \infty$. Schematically the response diagram, now a plot of y at $x = 0$ against ϕ , is the same as in Figure 1, with the same stability properties [2]. On the lower branch the expansions (2.3) still prevail, leading to the problem

$$y_{1xx} + \phi_1 \exp y_1 = 0, \quad y_{1x}(0) = y_1(0) = 0 \quad (3.3)$$

whose solution

$$y_1(x) = H(x; \phi_1) \quad (3.4)$$

can be represented parametrically by the equations

$$H = 2 \ln[\cosh \alpha \operatorname{sech}(\alpha x)], \quad \phi_1 = 2\alpha^2 \operatorname{sech}^2 \alpha, \quad 0 \leq \alpha \leq \alpha_c. \quad (3.5)$$

(Schematically, Figure 2 also represents the graph of $y_1(0)$ against ϕ_1 .)

The critical value α_c is given by

$$\alpha_c \tanh \alpha_c = 1 \quad (\alpha_c \approx 1.2)$$

whence

$$\phi_{1c} \approx 0.88, \quad y_{1c}(0) \approx 1.187.$$

The analysis in [11] also shows that at the point D on the upper branch (Figure 1),

$$y_D(0) = 1 + \beta - \text{est} \quad (3.6)$$

In fact, $y_D(x) = 1 + \beta - \text{est}$ throughout the domain, except for an exponentially thin layer at $x = 1$.

We shall find that the similarity between the static behaviors of the lumped and the distributed systems also extends to the dynamic responses due to slow variation of ϕ . Before pursuing that question, however, we digress for a brief look at the linear stability problem for the lower branch. This problem can be shown to yield the following leading-order eigenvalue problem in the limit $\gamma \rightarrow \infty$:

$$U'' + (\phi_1 \exp y_1)U - \Lambda U = 0, \quad U'(0) = U(1) = 0 \quad (3.7)$$

(Equation (3.7) can be derived most simply by reinstating the time-derivative $y_{1\tau}$ in (3.3), linearizing about the steady state, and seeking solutions of the type $U(x) \exp(\Lambda \tau)$.) Clearly, the eigenvalues Λ_i and the corresponding eigenfunctions $U_i(x)$ of this Sturm-Liouville problem depend upon ϕ_1 . For later use, we note two properties of (3.7). First, all Λ_i are negative for $\phi_1 < \phi_{1c}$, as a consequence of the asymptotic stability of the lower branch. In particular, therefore, $\Lambda = 0$ is not an eigenvalue for $\phi_1 < \phi_{1c}$. Second, $\Lambda = 0$ is an eigenvalue at the critical point $\phi_1 = \phi_{1c}$, because that is where the exchange of stabilities occurs. The corresponding eigenfunction is given by

$$u_{20}(x) = 1 - \alpha_c x \tanh(\alpha_c x) \quad . \quad (3.8a)$$

Incidentally, another (linearly independent) solution of the differential equation in (3.7) is

$$u_{10}(x) = \frac{1}{\alpha_c} \tanh(\alpha_c x) \quad . \quad (3.8b)$$

Turning now to the dynamic problem, we again employ the slow time $t = \delta\tau$, let $y = y(x, t)$ and rewrite (3.1a,b) as

$$\delta y_t = y_{xx} + (\beta\gamma)^{-1} \phi \exp(\gamma - \gamma/y), \quad 0 < x < 1 \quad , \quad (3.9a)$$

$$y_x(0, t) = y(1, t) = 1 \quad , \quad (3.9b)$$

and again take the initial condition, at $t = t_A < 0$, to be that corresponding to point A on the lower branch (Figure 1). The prescription (2.10) for ϕ still holds, but now we let

$$\phi_1(t) = \phi_{1c} [1 + t + O(t^2)] \quad \text{as } t \rightarrow 0 \quad . \quad (3.10)$$

The corresponding behavior of the parameter α , appearing in (3.5), is

$$\alpha(t) = \alpha_c - (-t)^{1/2} - \frac{1}{3\alpha_c} t + O[(-t)^{3/2}] \quad \text{as } t \rightarrow 0^- \quad . \quad (3.11)$$

This result will be found useful in future computations.

As in the lumped example, the evolution of the solution is again followed through several stages.

3.1 Pre-critical Solution

Expecting y to stay close to unity prior to criticality, we substitute

$$y = 1 + \gamma^{-1} z(x, t) \quad (3.12)$$

into (3.9a,b) to get

$$\delta z_t = z_{xx} + \phi_1 e^z + O(\gamma^{-1}), \quad z_x(0,t) = z_x(1,t) = 0. \quad (3.13)$$

For $\delta \gg \gamma^{-1}$, we assume the expansion

$$z = z_1 + \delta z_2 + o(\delta) \quad (3.14)$$

and thereby obtain, for z_1 , the problem

$$z_{1xx} + \phi_1 \exp z_1 = 0, \quad z_{1x}(0,t) = z_{1x}(1,t) = 0.$$

Comparison with (3.3) yields the pseudo-steady solution

$$z_1(x,t) = H(x; \phi_1(t)). \quad (3.15)$$

Application of the asymptotic expressions (3.10) and (3.11) into the definition (3.5) of H then shows that

$$z_1 = z_{1c}(x) - \frac{2}{\alpha_c} (-t)^{1/2} u_{20}(x) + O(t) \quad \text{as } t \rightarrow 0^-, \quad (3.16)$$

where

$$z_{1c}(x) = 2 \ln[\cosh \alpha_c \operatorname{sech}(\alpha_c x)] , \quad (3.17)$$

and $u_{20}(x)$ has already been introduced in (3.8a). The behavior (3.16), analogous to the lumped result (2.19), demonstrates that (3.15) is not valid beyond $t = 0$.

It is found that z_2 satisfies

$$z_{2xx} + (\phi_1 \exp z_1) z_2 = z_{1t}, \quad z_{2x}(0,t) = z_{2x}(1,t) = 0, \quad t < 0. \quad (3.18)$$

This nonhomogeneous problem yields a unique z_2 , as shown by the following argument. The homogeneous problem corresponding to (3.18) is identical to the eigenvalue problem (3.7) for $\Lambda = 0$ and for $\phi_1 < \phi_{1c}$, and therefore has

only the trivial solution (see the remark about zero not being an eigenvalue for $\phi_1 < \phi_{1c}$, made following (3.7)). Hence z_2 is unique, and has the representation

$$z_2(x,t) = a(t)u_2(x,t) + \int_0^x [u_1(x,t)u_2(\xi,t) - u_1(\xi,t)u_2(x,t)]z_{1t}(\xi,t)d\xi. \quad (3.19)$$

Here,

$$a(t) = -[u_2(1,t)]^{-1} \int_0^1 [u_1(1,t)u_2(\xi,t) - u_1(\xi,t)u_2(1,t)]z_{1t}(\xi,t)d\xi$$

and the $u_i(x,t)$ satisfy the homogeneous differential equation

$$u_{i_{xx}} + [\phi_1(t) \exp\{z_1(x,t)\}]u_i = 0 \quad (3.20a)$$

and the initial conditions

$$u_{1x}(0,t) = u_{2x}(0,t) = 1; \quad u_1(0,t) = u_2(0,t) = 0. \quad (3.20b)$$

(The remarks made at the end of Section 2.1 about satisfaction of initial conditions by z_1 and z_2 apply here as well.) The asymptotic nature of u_1 and u_2 is investigated in the Appendix and the results are

$$u_1(x,t) = u_{10}(x) + (-t)^{1/2}u_{11}(x) + o(t), \quad (3.21a)$$

$$u_2(x,t) = u_{20}(x) + (-t)^{1/2}u_{21}(x) + o(t), \quad \text{as } t \rightarrow 0^-. \quad (3.21b)$$

The functions u_{11} and u_{21} have been defined in the Appendix, while u_{10} , u_{20} were introduced in (3.8a,b). With these expressions in hand, (3.19) can be expanded for small t and the result is

$$z_2(x,t) = \frac{1}{3\alpha_c^2} (t)^{-1} u_{20}(x) + o[(-t)^{-1/2}] \quad \text{as } t \rightarrow 0^-, \quad (3.22)$$

which is analogous to (2.20). Thus, the pre-critical expansion (3.14) becomes disordered in much the same way as its lumped counterpart (2.15) did, and we are led to the transition solution.

3.2 Transition Solution

The transition time scale s is now defined by

$$t = -\delta^{2/3} b^{-1} s, \quad (3.23)$$

where the $O(1)$ constant b will be chosen later, in a way that simplifies algebra. When the above stretching, and the assumed transition expansion

$$z = z_{1c}(x) + \delta^{1/3} v_1(x,s) + \delta^{2/3} v_2(x,s) + \delta v_3(x,s) + o(\delta), \quad (3.24)$$

are fed into (3.13), the following equations for the v_i emerge:

$$v_{1xx} + (\phi_{1c} \exp z_{1c}) v_1 = 0, \quad (3.25a)$$

$$v_{2xx} + (\phi_{1c} \exp z_{1c}) v_2 = -b v_{1s} - (\phi_{1c} \exp z_{1c}) (-b^{-1} s + \frac{1}{2} v_1^2), \quad (3.25b)$$

$$v_{3xx} + (\phi_{1c} \exp z_{1c}) v_3 = -b v_{2s} - (\phi_{1c} \exp z_{1c}) (v_1 v_2 + \frac{1}{6} v_1^3 - b^{-1} s v_1). \quad (3.25c)$$

Each v_i is, of course, subject to the boundary conditions

$$v_{ix}(0,s) = v_{ix}(1,s) = 0; \quad i = 1, 2, 3. \quad (3.26)$$

The problem for v_1 can be solved immediately to yield

$$v_1(x,s) = f_1(s) u_{20}(x) \quad (3.27)$$

where the "amplitude function" $f_1(s)$ is to be determined by requiring that the nonhomogeneous equation (3.25b), subject to (3.26), have a solution. This requirement leads to the orthogonality condition

$$\int_0^1 [-bf_1'(s)u_{20}(x) - \{\phi_{1c} \exp z_{1c}(x)\} \{-b^{-1}s + \frac{1}{2} f_1^2(s)u_{20}^2(x)\}u_{20}(x)dx] ,$$

which, upon the evaluation of appropriate integrals, reduces to the differential equation

$$bf_1'(s) = 3b^{-1}s - \frac{3}{4} \alpha_c^2 f_1^2(s), \quad s < \infty .$$

The condition

$$f_1 \rightarrow -\frac{2}{\alpha_c} b^{-1/2} s^{1/2} - \frac{b}{3\alpha_c^2} (s)^{-1} \quad \text{as } s \rightarrow \infty$$

is provided by the pre-critical solution upon matching. Thus, the familiar Riccati problem emerges again (cf. (2.25a,b)). In fact, the choice

$$b = (9\alpha_c^2/4)^{1/3}$$

leads to the solution

$$f_1(s) = 3(9\alpha_c^2/4)^{-2/3} Ai'(s)/Ai(s) , \quad (3.28)$$

thereby determining v_1 completely, once (3.28) is substituted into (3.27).

It is now possible to write down the solution to (3.25b) and (3.26). The resulting expression for v_2 will contain $f_2(s)u_{20}(x)$ as the complementary function. By appealing to the solvability requirement on the v_3 -equation, (3.25c), and by matching with the pre-critical solution, we can show that f_2 satisfies a differential problem (analogous to that in (2.28)) which can be solved. The relevant calculations were made, because they are needed to determine the leading-order solution at the next stage. However, although straightforward, they are too cumbersome to report here.

As s approaches s_0 , f_1 explodes (see (2.27)), leading us to the next stage of solution development.

3.3 Post-critical and Jump Solutions

Following the treatment of Section 2.3, the new time variable ρ is defined by

$$s = s_0 - b\delta^{1/3}(\rho - \rho_0) ,$$

or equivalently by

$$t = -\delta^{2/3}b^{-1}s_0 + \delta(\rho - \rho_0) ,$$

where ρ_0 is the yet unknown shift as before, and z is assumed to have the expansion

$$z = w_1(x, \rho) + o(1) . \quad (3.29)$$

Then, (3.13) provides the leading-order problem

$$w_1 = w_{1_{xx}} + \phi_{1_c} \exp w_1, \quad 0 < x < 1, \quad \rho > -\infty , \quad (3.30a)$$

$$w_{1_x}(0, \rho) = w_1(1, \rho) = 0 , \quad (3.30b)$$

for which the initial condition

$$w_1 = z_{1_c}(x) - \frac{4}{3\alpha_c^2} u_{20}(x) + o(\rho^{-1}) \quad \text{as } \rho \rightarrow -\infty \quad (3.30c)$$

comes from matching with two-terms of the transition expansion (3.24). In order to determine the shift ρ_0 and to fix the origin of ρ in the w_1 problem (i.e. to fix the counterpart of the constant $\bar{\rho}_0$ appearing in (2.34)), matching with three terms of (3.24) is needed, and this is where the knowledge of $v_2(x, s)$ is required.

We now stress two aspects of w_1 . First, it evolves at a constant value ϕ_{1_c} of ϕ_1 . Second, it measures the departure of y from unity on the $O(\gamma^{-1})$ scale; this is shown by the asymptotic expression

$$y = 1 + \gamma^{-1} w_1(x, \rho) + o(\gamma^{-1}) \quad (3.31)$$

obtained by substituting (3.29) into (3.12). Therefore, w_1 plays the same role as the induction-period solution of the author's earlier paper [5], where transition from an extinguished to the ignited state is studied at fixed β ; also see [6]. In fact, as we shall see, the entire analysis of [5] applies here, as did Kassoy's fixed ϕ analysis [8] in the lumped case.

Figure 3 shows the numerical solution of (3.30a,b,c), obtained by using the package PDECOL [12]. This package employs B-splines for spatial discretization, and then integrates the resulting ordinary differential equations with a Gear solver. Integration was begun at a large negative value of ρ . We find that initially the solution develops slowly, but then w_1 begins to rise rapidly near $x = 0$ while variations continue to be leisurely in the rest of the domain. Eventually, at a definite $\rho = \rho_\infty$, $w_1(0, \rho)$ becomes unbounded (compare with Figure 3 of [5]).

The explosive behavior of w_1 in the thin boundary layer at $x = 0$ can be analyzed; this was done in [5] and a logarithmic singularity (cf. (2.37)) was revealed. This singularity marks the breakdown of (3.31), and further development is exponentially fast, as it was in the lumped case. For full details the reader is referred to [5]. Summarizing briefly, a rapidly shrinking hot spot of growing intensity developed at $x = 0$. When y reaches the value $1 + \beta$ there, the hot spot detaches from the left boundary and moves into the interior of the domain as a well-defined reaction wave, still traveling exponentially fast and leaving behind a burnt zone at constant $y = 1 + \beta$. Just before the right boundary is reached, the wave quickly comes to rest (on the exponentially fast scale) to accommodate the boundary condition at $x = 1$. In other words, the jump to point D in Figure 1 is now complete (see (3.6)). Further movement along the upper branch will again be governed by the slow variable t , much in the manner of the pre-critical solution.

4. CONCLUDING REMARKS

The asymptotic analysis has concentrated on the behavior of the systems as the parameter ϕ , a measure of the rate of reaction, passes slowly through the ignition criticality. It is shown that the solution follows the lower branch at the slow scale $\delta\tau$ (where τ is the reference scale, i.e. the residence time for lumped systems and diffusion time for distributed systems), passes through criticality at the slightly faster scale $\delta^{1/3}\tau$, and goes through the initial stage of the jump at the scale τ . Most of the jump, however occurs at an exponentially fast scale (in γ), and the subsequent travel along the upper branch occurs again at the slow scale $\delta\tau$. The similarities between the responses of the lumped and distributed systems are clearly demonstrated.

From a practical viewpoint, the ignition problem considered here is probably of greater relevance in combustion, where increase of ϕ may be associated with increase of pressure. On the other hand, in chemical engineering the extinction problem might have more significance, where decrease in ϕ could be the result of a decline in the efficiency of a catalyst. A similar treatment would apply there, but the extinction jump would be much less dramatic.

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APPENDIX

Here we are concerned with the solutions $u_i(x,t)$, $i = 1,2$, of the equation

$$u_{xx} + F(x,t) = 0 \quad (A.1)$$

subject to the initial conditions

$$u_{1x}(0,t) = 1, \quad u_{1x}(0,t) = 0; \quad u_{2x}(0,t) = 0, \quad u_{2x}(0,t) = 1 \quad (A.2)$$

The function F appearing in (A.1) is defined by

$$F(x,t) = \phi_1(t) \exp[z_1(x,t)]$$

which, from (3.15) and (3.5), is seen to be

$$F(x,t) = 2\alpha^2 \operatorname{sech}^2(\alpha x) \quad (A.3)$$

Of particular interest is the behavior of u_1 and u_2 as $t \rightarrow 0^-$. First, we note that at $t = 0$, $\alpha = \alpha_c$ so that $F(x,0) = 2\alpha_c^2 \operatorname{sech}^2(\alpha_c x)$. Then, it is easily checked that (A.1) and (A.2) have the solutions

$$u_1(x,0) = u_{10}(x) = \frac{1}{\alpha_c} \tanh(\alpha_c x) \quad ,$$

$$u_2(x,0) = u_{20}(x) = 1 - \alpha_c x \tanh(\alpha_c x) \quad .$$

These functions have already appeared in (3.8a,b). Now, in view of the asymptotic expression (3.11) for α , (A.3) gives

$$F(x,t) = 2\alpha_c^2 \operatorname{sech}^2(\alpha_c x) \left[1 - \frac{2}{\alpha_c} (-t)^{1/2} u_{20}(x) + o(t) \right] \quad \text{as } t \rightarrow 0^- \quad , \quad (A.4)$$

suggesting the expansions

$$u_i(x,t) = u_{i0}(x) + (-t)^{1/2} u_{i1}(x) + o(t) \quad \text{as } t \rightarrow 0^-; \quad i = 1,2 \quad (A.5)$$

When (A.4) and (A.5) are substituted into (A.1) and (A.2), we find that the

$u_{il}(x)$ satisfy

$$u_{il}'' + 2\alpha_c^2 \operatorname{sech}^2(\alpha_c x) u_{il} = 4u_{i0} u_{20} \alpha_c \operatorname{sech}^2(\alpha_c x); \quad i = 1, 2, \quad ,$$

$$u_{il}'(0) = u_{il}(0) = 0 \quad ,$$

leading to the solutions

$$u_{il}(x) = \int_0^x 4\alpha_c u_{i0}(\xi) u_{20}(\xi) \operatorname{sech}^2(\alpha_c \xi) [u_{10}(x) u_{20}(\xi) - u_{10}(\xi) u_{20}(x)] d\xi; \quad i = 1, 2 \quad .$$

Upon evaluation of the appropriate integrals, we find that

$$u_{11}(x) = \frac{1}{\alpha_c^2} [\tanh(\alpha_c x) - \alpha_c x \operatorname{sech}^2(\alpha_c x)] \quad ,$$

$$u_{21}(x) = x [\tanh(\alpha_c x) + \alpha_c x \operatorname{sech}^2(\alpha_c x)] \quad .$$

FIGURE CAPTIONS

Figure 1. The steady-state response

Figure 2. The lower branch

Figure 3. The numerically-computed plot of $w_1(x, \rho)$.

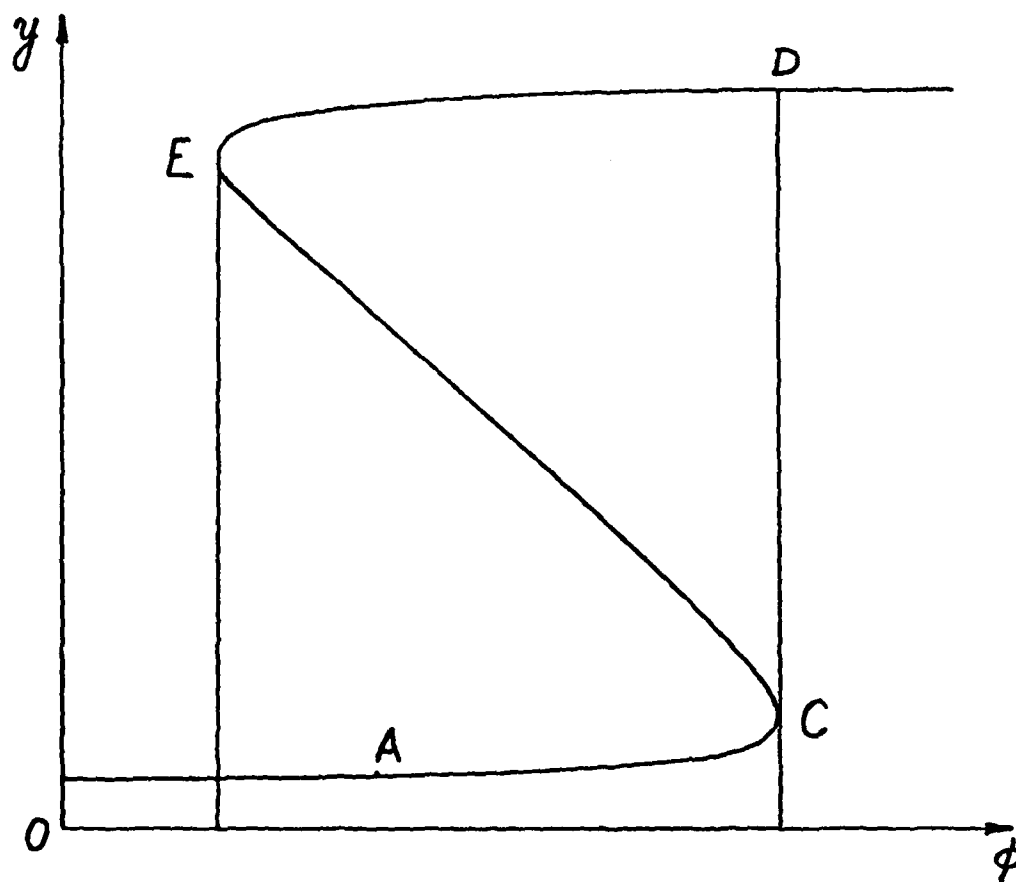


Fig. 1

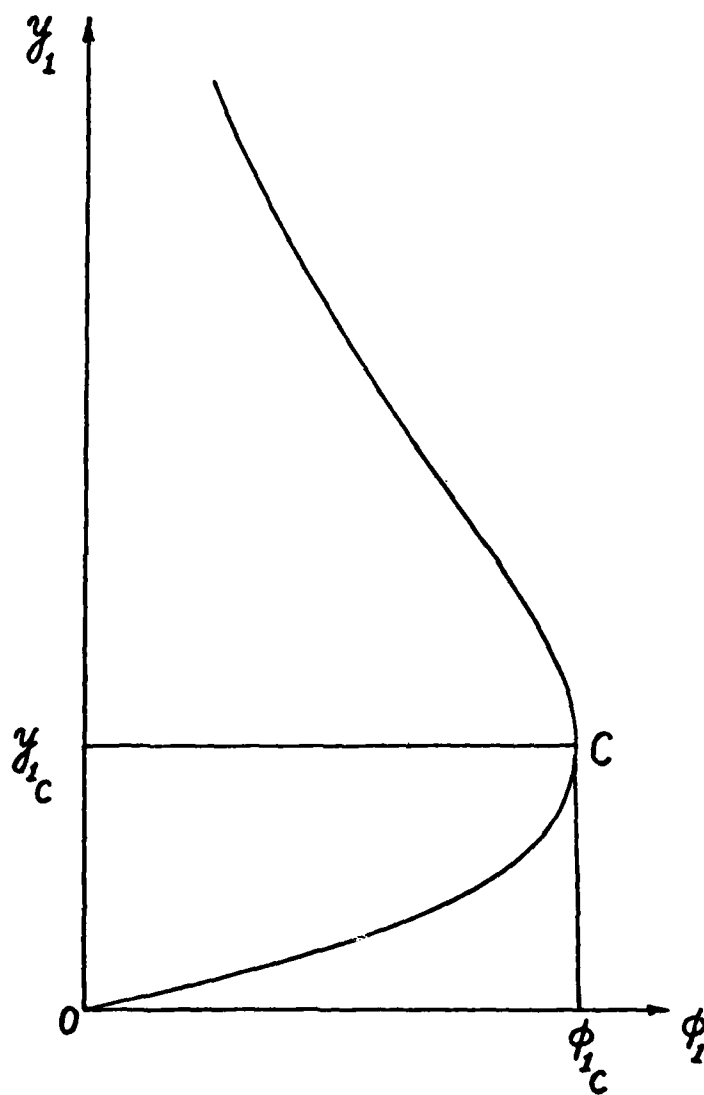


FIG. 2

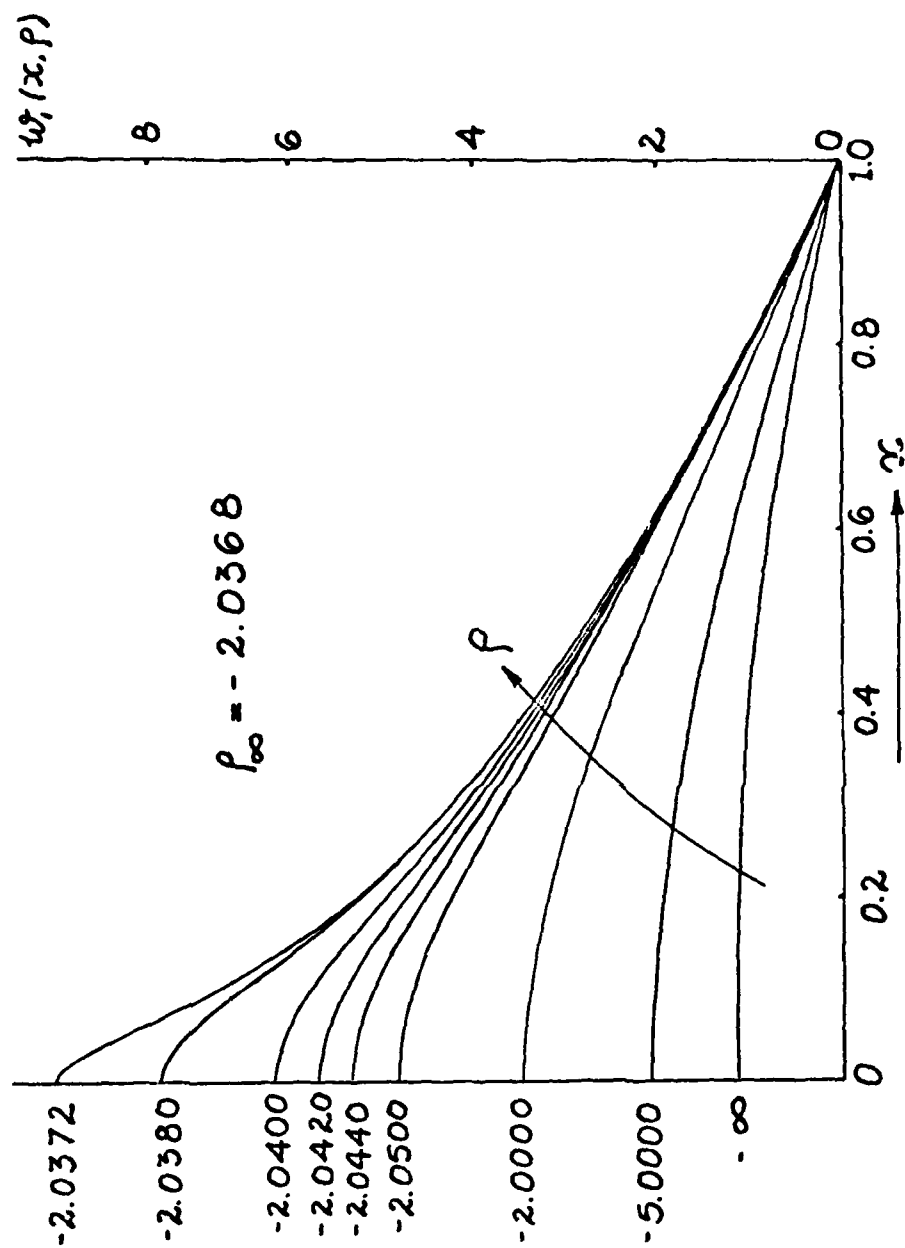


Fig. 3

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